



Carbon coated lithium cobalt phosphate for Li-ion batteries: Comparison of three coating techniques

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HIGHLIGHTS

- ▶ Three techniques are adopted to coat carbon on LiCoPO₄ materials.
- ▶ The LiCoPO₄/C processed via deposition shows a homogeneous carbon coating.
- ▶ LCP-deposition delivers a high capacity of 130 mA h g⁻¹ with favorable cyclability.
- ▶ A uniform carbon layer is the key to a high and stable electrochemical performance.

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ABSTRACT

Three techniques, i.e., pyrolysis of sucrose, spray of acetylene black, and propane vapor deposition, are adopted to coat carbon onto the surface of LiCoPO₄ particles, and their effects are compared. The LiCoPO₄/C composites are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS). The results show that the coating techniques determine the property of carbon films formed on the surface of LiCoPO₄ particles, which further affect the performance of LiCoPO₄. A complete and homogeneous carbon layer is the key to a high electrochemical activity and stable cycle performance. Among these LiCoPO₄/C composites, the material processed via the deposition technique shows a more uniform carbon layer than that of the others, thus it exhibits a large reversible capacity of 130 mA h g⁻¹ with favorable cyclability and rate capability in the voltage range of 3.0–5.0 V.

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1. Introduction

Owing to the intrinsically stable nature and good electrochemical properties, olivine structured LiMPO₄ (M = Fe, Mn, Co, Ni) materials have received a lot of attention since their discovery as cathode materials for Li-ion batteries in 1997 [1]. Among them, LiCoPO₄ has recently received particular attention due to its high redox potential of 4.8 V (vs. Li/Li⁺, unless otherwise stated) and thus high energy density of 800 W h kg⁻¹, which is essential for batteries to be used in large-format power and energy storage systems. However, the high energy density is difficult to attain, or otherwise it degrades quickly because of poor kinetics and instable cyclability of LiCoPO₄ [2–4]. When operating at a high voltage about 5 V, severe side reaction of electrolyte degradation occurs at

electrode/electrolyte interphase, leading to a drastic capacity fading upon cycling [5–8]. For example, Bramnik et al. reported an initial discharge capacity of 70 mA h g⁻¹, and only 10 mA h g⁻¹ remaining in the 20th cycle [6]. Rabanal et al. also demonstrated a rapid capacity loss for LiCoPO₄ from 80 mA h g⁻¹ to 40 mA h g⁻¹ after 20 cycles, and further to 10 mA h g⁻¹ in the 40th cycle [8].

A variety of strategies have been developed to improve the electrochemical activity of LiCoPO₄, most of which follow the similar way as the modification of LiFePO₄ material by carbon coating and size reducing [9–14]. These methods enhance the kinetics of LiCoPO₄ and stabilize the interphase as well. The LiCoPO₄/C core/shell nanocomposite demonstrated high reversible capacities of 144 and 136 mA h g⁻¹, as reported by Li et al. [11] and Taniguchi et al. [12], respectively. However, fast capacity degradation was observed in both cases, due probably to the insufficient carbon layer that does not fully cover the surface of all particles. Therefore, electrolyte can easily access the particle surfaces and trigger side reactions. To improve the cyclability, Shui et al. reported a LiCoPO₄ composite consisting of Li₃PO₄ and Co₃O₄ to achieve

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a high retention of 86% upon 35 cycles [13]. Alternatively, Jang et al. reported a $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4/\text{LiFePO}_4$ core/shell structure, and obtained 70% retention after 20 cycles. It is supposed that both LiFePO_4 and Li_3PO_4 components significantly suppress the surface side reaction, and thus improve the cycling behavior [14]. The major problem is that neither Li_3PO_4 nor LiFePO_4 is an electronic conductor, which may affect the capacity delivery and rate capability. On the other hand, ion doping has been proven to be an effective way to enhance conductivity and thus the electrochemical property of LiCoPO_4 [15,16]. Particularly, Allen et al. have proposed a Fe^{3+} -doped structure to suppress the reactivity of LiCoPO_4 , and successfully raised the cycling stability up to 500 cycles with 80% capacity retention [17]. However, the discharged capacity and cycling rate data are not available.

Among versatile modifications, an efficient coating layer seems to be critical to a high-performance and stable LiCoPO_4 electrode. Particularly, coating by carbon is promising because it addresses the conductivity and stability issues simultaneously. However, previous work often adopted an ex situ coating method by ball milling LiCoPO_4 with carbon black [10–12]. Due to limitation of this method, although partial surfaces are covered, the coverage is far from complete and uniform. Consequently, the coated samples still exhibit a fast fading in capacity. In this work, we adopt three techniques to coat LiCoPO_4 with carbon and compare their effect on the formed LiCoPO_4/C composites. The structure, morphology, homogeneity of coating layer, and electrochemical activities of the LiCoPO_4/C composites are examined in detail. These results are correlated to illustrate how the coating techniques can determine the quality of the carbon layer and the performance of LiCoPO_4 .

2. Experimental

Pure LiCoPO_4 material was prepared by an aqueous precipitation route using LiOH , CoSO_4 , and H_3PO_4 as starting materials following Delacourt's report [18]. In a typical processing, a 10 mmol CoSO_4 aqueous solution was mixed with 10 mmol H_3PO_4 at vigorous agitation. A LiOH solution was added dropwise to the mixture until the pH value reaching ~ 7 . After filtration, the precipitate was carefully collected and dried. Finally, the resultant purple powder was heated at 600°C for 5 h to obtain a crystalline phase. The phase was identified by X-ray diffraction as a pure olivine structure.

To fabricate carbon coated LiCoPO_4 samples, a static pyrolysis technique and two dynamic techniques of spray and deposition were adopted to coat about 5 wt.% carbon. Accordingly, the resultant LiCoPO_4/C products are denoted as LCP-pyrolysis, LCP-spray, and LCP-deposition, respectively. Fig. 1 schematically shows the processes. For the pyrolysis approach, 1.0 g LiCoPO_4 powder was mixed with 0.23 g sucrose in a planetary mill, and then the milled mixture was heated at 650°C for 1 h under Ar flow (Schematic 1a in Fig. 1). During the heating process, sucrose was carbonized and coated on the surface of LiCoPO_4 particles. As for the spray method, typically, a suspension containing 5 wt.% acetylene black and 1 wt.% polyvinyl alcohol (PVA) was fed into a coating facility (Powrex, Japan) where LiCoPO_4 powder was rotated. By spraying, the acetylene black was loaded onto the surface of material particles (Schematic 1b in Fig. 1). Then the admixture was heated at 600°C to carbonize residual PVA. For processing LCP-deposition sample, 0.6 g LiCoPO_4 material was loaded into a home-made rotary kiln, while a continuous propane flow was also directed into the kiln. The furnace was kept at 650°C for 1 h when the propane was degraded to carbon and deposited onto the LiCoPO_4 material (Schematic 1c in Fig. 1). Note that heating at 650°C is essential to obtain highly conductive carbon degraded from organic precursors [19], while the temperature does not result in substantial reduction of LiCoPO_4 [9].

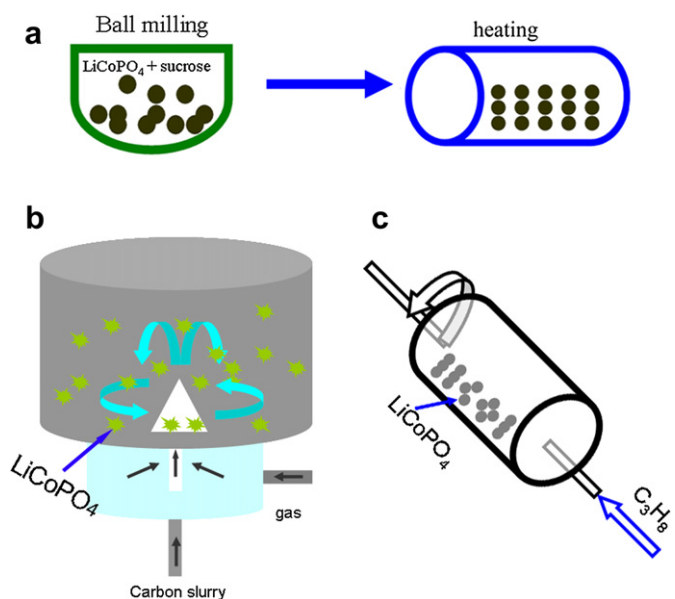


Fig. 1. Schematic presentation of the three techniques used for carbon coating on LiCoPO_4 .

The structure of the LiCoPO_4/C composite was identified by X-ray diffraction (XRD) using a Rigaku Dmax-2400 automatic diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$). The diffraction data were collected from 10 to 100° employing a step scanning procedure at an interval of 0.02° with a count time of 2 s [20]. The structural analysis was performed with the Rietveld method on the program Rietan-2000 [21]. The morphology of the product was examined by scanning electron microscopy (SEM, JEOL JSM-6390). Carbon coating layer was examined by transmission electron microscopy (TEM, FEI Tecnai G2 T20). Element mapping was recorded on an energy dispersive X-ray spectroscopy (EDS, Oxford).

The electrochemical properties of the LiCoPO_4 materials were examined using 2032 coin cells. The cell comprises a lithium foil anode, a polypropylene separator and a composite cathode sheet consisting of 80 wt.% active material, 10 wt.% carbon black, and 10 wt.% polyvinylidene fluoride, with a typical material loading of 3 mg cm^{-2} . The coin cells were assembled in an Ar-filled glove box (MBraun) with both O_2 and H_2O concentration below one ppm. The organic electrolyte is 1 mol L^{-1} LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 by volume). All the cells were tested on a Land battery program-controlled test system in the voltage range of 3.0 – 5.0 V at room temperature. The cells were first activated by performing one cycle before subject to various tests.

Electrochemical impedance spectroscopy (EIS) was carried out using a Solartron SI 1280B electrochemical unit. The spectra were measured with the frequency ranging from 20 kHz to 0.1 Hz and the oscillation voltage being 10 mV .

3. Results and discussion

3.1. Structure

XRD spectra of the carbon-coated LiCoPO_4 materials are shown in Fig. 2a. It can be seen that all the patterns display well resolved diffraction peaks, which can be indexed to olivine LiCoPO_4 (PDF #32-0552). Peaks due to carbon are not visible, because of the low degree of crystallinity. Structural analysis based on Rietveld refinement was implemented on the recorded XRD data. Fig. 2b

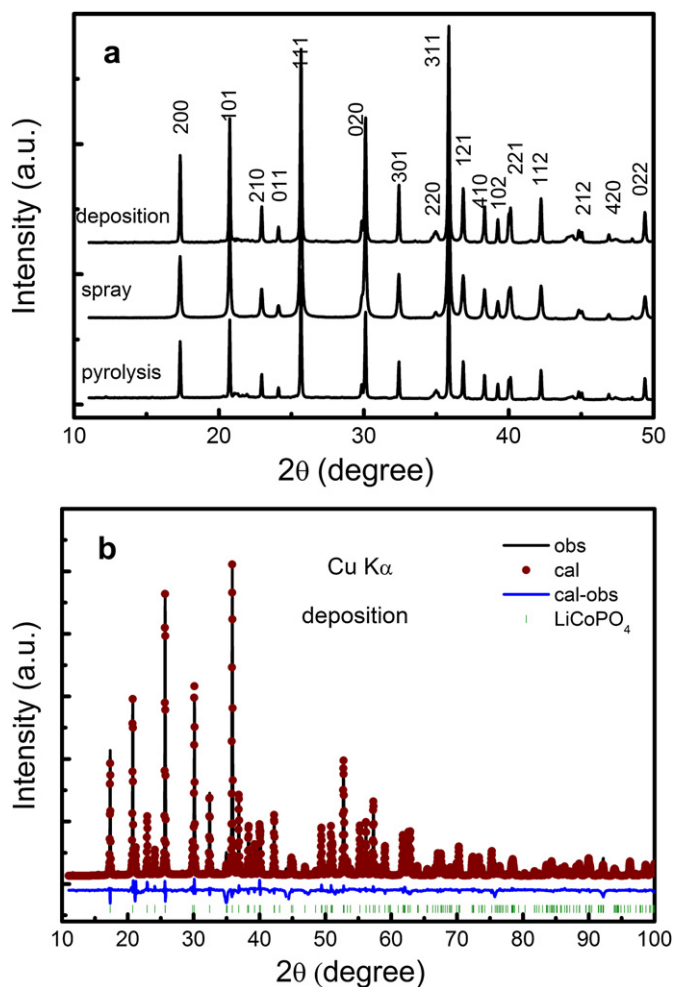


Fig. 2. (a) XRD patterns of the carbon-coated LiCoPO_4 materials, and (b) Rietveld refinement results of the LCP-deposition sample.

presents the refinement result of the typical LCP-deposition sample. The calculated pattern matches the observed one quite well, implying the reliability of the refinement. The refinement reveals lattice parameters of $a = 1.0201$ (2) nm, $b = 0.5923$ (1) nm, $c = 0.4700$ (5) nm, and accordingly $V = 284.01 \text{ nm}^3$ for LCP-deposition, in good agreement with previous reports [4,7,12]. The other two samples exhibit rather similar lattice parameters, signifying that carbon coatings exert little impact on the olivine structure.

3.2. Morphology

The morphologies of LiCoPO_4/C materials examined by SEM are illustrated in Fig. 3. The pure LiCoPO_4 prepared via the solution route is comprised of peanut-shape particles with smooth surface. The average particle size is about 250 nm in width and 600 nm in length (Fig. 3a). After carbon coating, the original shape and size are nearly maintained for the LiCoPO_4/C materials except for LCP-pyrolysis, where large agglomeration is observed (Fig. 3b). This aggregation is probably resulted from fusion of grains at high temperatures when they are not well covered by heterogeneous carbon. In contrast, such agglomeration is barely visible for LCP-spray (Fig. 3c) and LCP-deposition (Fig. 3d), possibly due to more uniform coating. To confirm the assumption, the samples were characterized by EDS. Fig. 4 compares the element mapping of

three LiCoPO_4/C composites. In the cases of LCP-spray and LCP-deposition, the element mapping of C matches that of Co, O, P well, indicating the coating of carbon is uniform. However, LCP-pyrolysis discloses an unmatched carbon contour, implying that static pyrolysis approach is not as effective as the other dynamic ones.

The samples were further characterized by high-resolution TEM to examine the surface coating layer. Fig. 5 shows TEM images of the LCP-deposition sample. It is clearly observed that a uniform carbon film is formed on the particle surface (Fig. 5a, marked by arrows). The film is homogeneous and complete, with a thickness of $\sim 4 \text{ nm}$ (Fig. 5b). This observation manifests the effectiveness of the deposition technique. It is worth noting that the LiCoPO_4 crystallite shows a lamellar structure with a d -spacing of 0.387 nm, consistent with the (210) peak of XRD pattern of olivine phase.

3.3. Charge and discharge

The charge and discharge profiles of the bare and three carbon coated materials at 10 mA g^{-1} current density are displayed in Fig. 6. All the electrodes display two sets of distinct plateau around 4.8 V over both charge and discharge process, indicating a stepwise behavior of Li extraction and reinsertion. Such phenomenon is quite different from other olivine materials like LiFePO_4 and LiMnPO_4 [1]. Ehrenberg et al. has proposed that the LiCoPO_4 phase evolution proceeds in two steps, firstly to an intermediate phase $\text{Li}_{0.7}\text{CoPO}_4$, and then to the CoPO_4 [22]. It is seen that all the modified samples exhibit a much improved electrochemical property than the bare one. Particularly, LCP-deposition delivers a reversible capacity of 130 mA h g^{-1} , about twice that of the bare material (70 mA h g^{-1}). It is worth noting that the capacity of LCP-deposition is comparable to those released in previous reports [12,16], even though LCP-deposition has a low carbon loading. This improvement can be ascribed to the enhanced electronic conductivity by carbon coating, which reduces polarization and facilitates charge transfer. The other two approaches seem to be not effective as the deposition one, as LCP-spray and LCP-pyrolysis display discharge capacities of 116 and 112 mA h g^{-1} , respectively.

One major challenge for LiCoPO_4 cathode is the instability in cycling, which probably results from various factors such as poor conductivity [8,9], solvent oxidation at high voltage [15], oxygen release [17], or amorphization induced by HF [23]. To investigate the effect of carbon film on the cyclability, the bare and coated LiCoPO_4 electrodes were galvanostatically cycled at 10 mA g^{-1} as shown in Fig. 7. The bare LiCoPO_4 exhibits a quite poor cycling behavior, consistent with previous reports [8,15]. After 30 cycles, it only retains 11% of capacity. In contrast, the LCP-deposition delivers a capacity of 103 mA h g^{-1} at the 30th cycle, and the retention is about 80%, superior to those found in other reports [8,12,15]. It is well known that the extent of capacity fading could be further diminished if a high current rate is used in cycling, because the electrolyte decomposition is time dependent [8]. The other two carbon coated samples exhibit a similarly improved behavior, even though they are not as efficient as LCP-deposition. After 30 cycles, LCP-pyrolysis and LCP-spray deliver capacities of 58 and 81 mA h g^{-1} , or 52% and 70% of their initial capacities, respectively.

It is therefore suggested that a uniform and robust carbon layer could efficiently enhance the cycling performance. This can be explained in terms of conductivity and stable electrode surface. It is known that the LiCoPO_4 particles experience the risk of losing electrical connection with current collector upon cycling due to repeated volume change if they are not well electrochemically wired by conductors. With perfect carbon decoration, such risk can be minimized, and the electronic contact can be maintained. On the other hand, the coating layer also stabilizes the delithiated CoPO_4

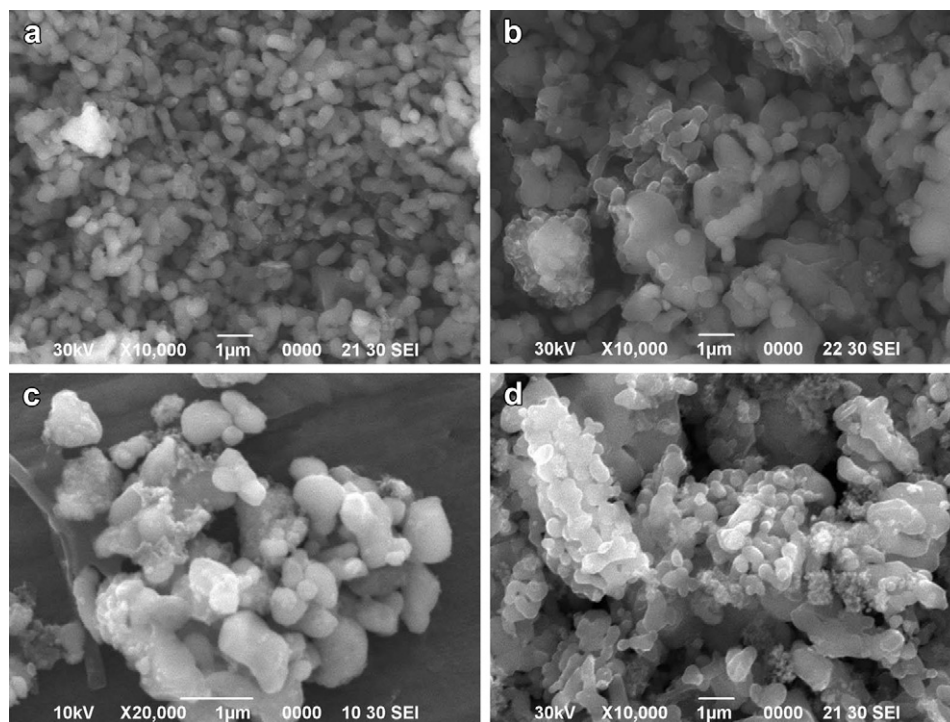


Fig. 3. SEM images of (a) pure LiCoPO_4 , (b) LCP-pyrolysis, (c) LCP-spray, and (d) LCP-deposition.

material and suppresses parasite reactions like electrolyte decomposition. The highly active Co^{3+} species can catalyze electrolyte decomposition, which accounts for the capacity loss of LiCoPO_4 over cycles. Under such circumstance, the charge current passing

the electrode does not extract Li ions but oxidize the solvents, leading to decreased real charge capacity than the rated one. In addition, side products may deposit onto the surface of LiCoPO_4 electrodes, which attributes to an increased resistance and

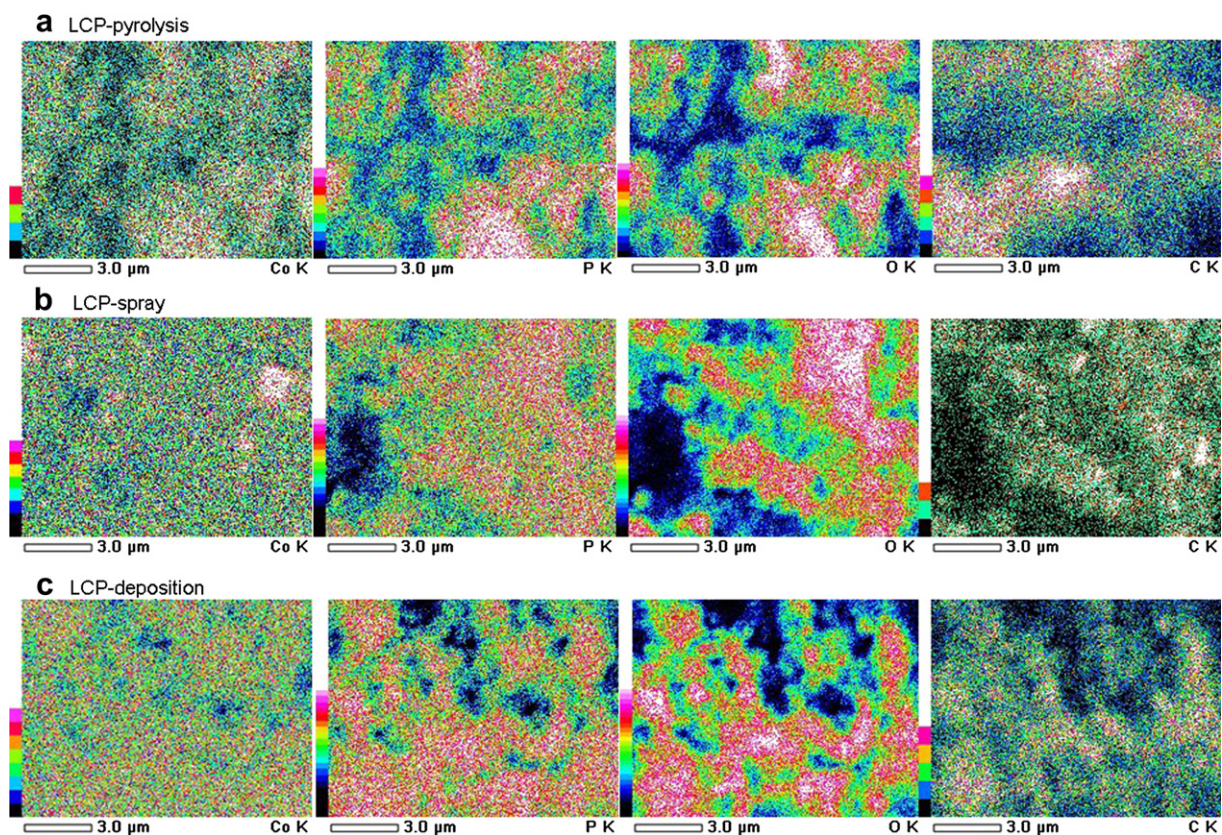


Fig. 4. Elemental mapping of Co, P, O, and C of (a) LCP-pyrolysis, (b) LCP-spray, and (c) LCP-deposition by EDS.

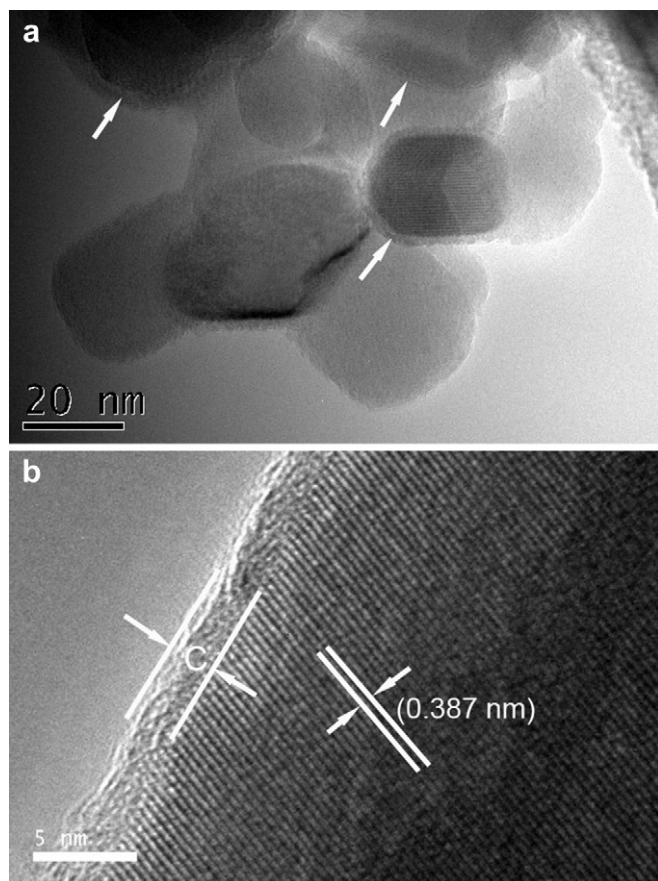


Fig. 5. (a, b) TEM images of LCP-deposition showing the carbon coating. The carbon layer is indicated by arrows in (a).

polarization. By pre-loading a carbon layer on the surface of LiCoPO_4 electrode, the Co^{3+} species was stabilized, and the cyclability was therefore enhanced.

To confirm the above hypothesis, cyclic voltammetry was conducted on the carbon black or pyrolytic carbon. Fig. 8 shows cyclic voltammogram of the carbon black electrode at a scan rate of 1 mV s^{-1} between 3 and 5.2 V. The carbon exhibits an inert response above 5.0 V, except for the appreciable anodic peak

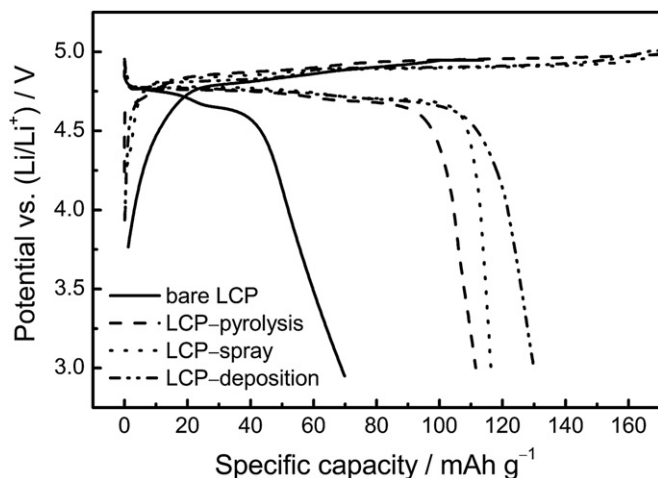


Fig. 6. Charge and discharge profiles of the bare and carbon-coated LiCoPO_4 materials at 10 mA g^{-1} between 3.0 and 5.0 V.

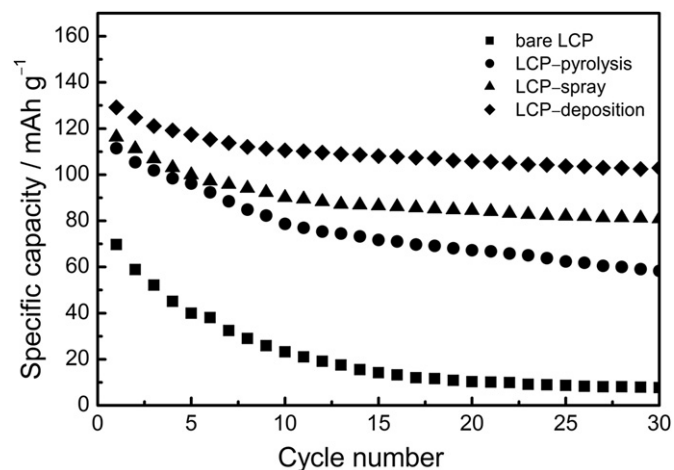


Fig. 7. Discharge capacity of the bare and carbon-coated LiCoPO_4 electrodes at 10 mA g^{-1} as a function of cycle number.

centered at 4.2 V. This peak, however, vanishes during the following cycles, indicating that it may be due to surface adsorbed species [24]. The intensity of the current response is several orders of magnitude below that of LiCoPO_4 electrode [25], implying that both electrochemical responses from electrolyte and carbon are negligible. Considering the large irreversible capacity occurred at LiCoPO_4 electrodes, it is reasonable to conclude that Co^{3+} may serve as a catalyst to accelerate the oxidation of electrolyte. This catalytic ability inherits from the strong electron-withdrawing capability of Co^{3+} ions, as it is revealed by XAS analysis [7].

3.4. Impedance

Fig. 9 shows Nyquist plots of the three coated electrodes measured under discharge at stages of before and after 10 cycles, respectively. All the spectra consist of a depressed semi-circle in the high and middle frequency range and a straight line in the low frequency. To analyze the measured impedance data, a modified “SCR” equivalent circuit (Fig. 10a) was constructed to simulate the impedance spectra [26]. The fitting was conducted using the Zview program, and some key parameters are tabulated in Table 1. The fitting parameter R_s represents the contact and solution resistance,

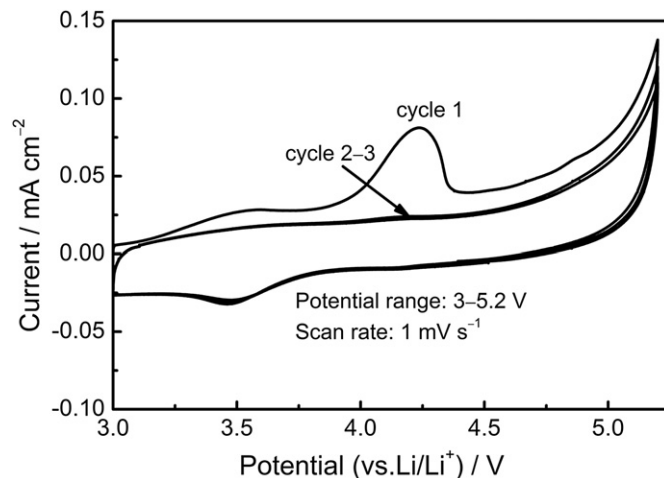


Fig. 8. Cyclic voltammogram of the carbon black electrode at 1 mV s^{-1} between 3.0 and 5.2 V.

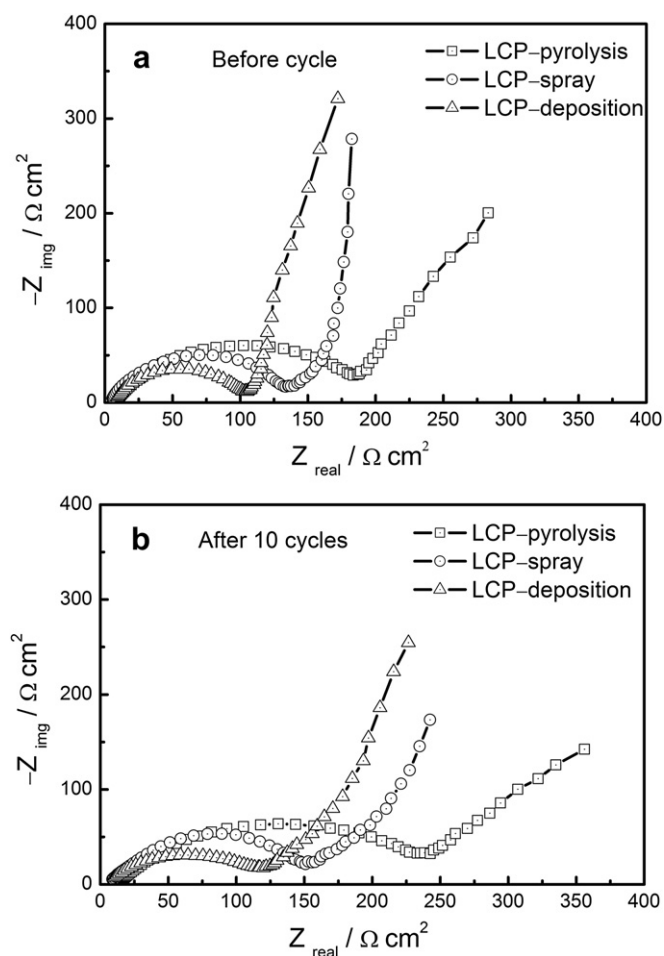


Fig. 9. Nyquist plots of electrochemical impedance spectra of the carbon-coated LiCoPO₄ electrodes (a) before cycle and (b) after 10 cycles.

R_f the membrane resistance due to surface films on Li anode and LiCoPO₄ cathode [27], R_{ct} the charge transfer resistance, CPE1 and CPE2 the constant phase elements related to Li movement across surface membrane and into electrode bulk, and C the double layer capacitance associated with charge transfer. The CPE is generally associated with the porous structure of electrode and inhomogeneous electrochemical reaction rates [26]. The simulation gave an acceptable match of χ^2 in the order of 10^{-4} for all cases, as it can be seen from Fig. 10b showing a typical fitting result of the impedance spectra of LCP-spray.

It is seen from Table 1 that the values R_s of three electrodes are close, probably because of the solution resistance and contact resistance are similar with same cell structure. However, their R_f values differ significantly from each other before and after cycles. Before cycling, the R_f of LCP-deposition is 99 $\Omega \text{ cm}^2$, which is less than that of LCP-spray (136 $\Omega \text{ cm}^2$), and only about one third of that of LCP-pyrolysis (285 $\Omega \text{ cm}^2$). The larger R_f indicates that a thicker surface film may form on the Li and LiCoPO₄ electrodes for LCP-spray and LCP-pyrolysis. Similarly, LCP-deposition also shows a minimum R_{ct} of 61 $\Omega \text{ cm}^2$, and it even decreases to 52 $\Omega \text{ cm}^2$ after 10 cycles. The impedance results correlate well with the galvanostatic test results and further suggest that this deposition technique is more suitable for carbon coating on LiCoPO₄ than the other two. It is noted that the slope of lines at low frequency decreases after cycling, possibly due to the variation of Li ion diffusion coefficient [26].

Since the same LiCoPO₄ active materials were used, and the amount of carbon loading is almost identical, the discrepancy in

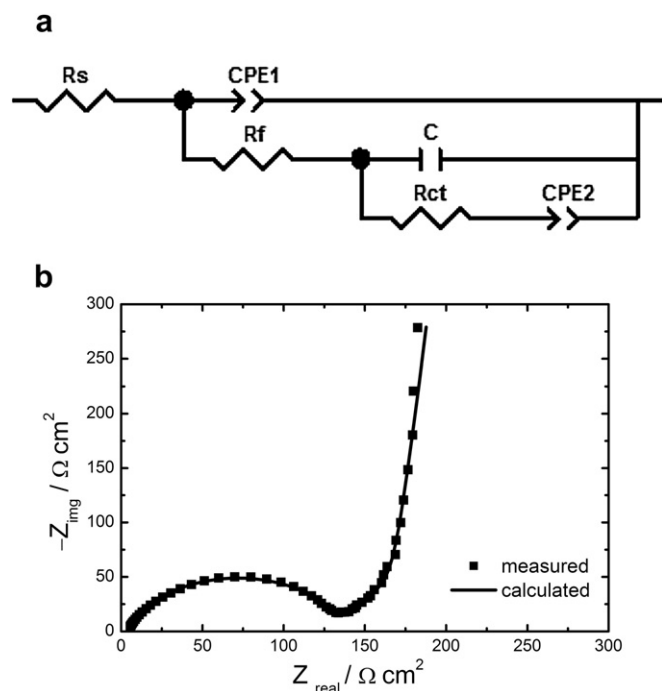


Fig. 10. (a) The equivalent circuit built for impedance simulation and (b) the fitting result of impedance spectra of LCP-spray.

performance is most possibly attributed to the quality of coated carbon such as completeness and homogeneity. It is proposed that a robust and homogeneous carbon layer is critical to the fast kinetics and good cycle life, as the carbon coating increases electronic conductivity and at the same time isolates the highly active delithiated CoPO₄ phase from electrolyte [28]. The SEM and EDS results show that the static pyrolysis route only results in a loose and inhomogeneous carbon layer, whereas the dynamic spray and deposition routes can lead to a compact and homogeneous coverage of carbon on LiCoPO₄ particles. The latter two methods seem more efficient and promising. Although these two dynamic techniques are generally engineerable, the deposition approach is more effective because it uses propane gas instead of acetylene black in solid particles as carbon sources. Analogous experiments have also reported by Wang et al., who demonstrated that the carbon film on LiMnPO₄ is more homogeneous by deposition rather than by ball-milling [29]. In addition, the well coated sample can avoid particle growth, as the heterogeneous carbon phase impedes the fusion of grains. It is well known that small particles could alleviate the sluggish mobility of both electron and ions in olivine phase by shortening the diffusion distance, thus it will lead to a high level of capacity and power capability.

Fig. 11 shows the discharge profile of LCP-deposition at different current density in examination of its power capability. At a moderate current of 50 mA g⁻¹, the discharge capacity is 109 mA h g⁻¹. When current increases to 150 and 300 mA g⁻¹, the capacities are 89 and 76 mA h g⁻¹, respectively. Although the rate

Table 1

Fitting parameters of the impedance spectra of the three LiCoPO₄/C electrodes. The symbolic slash (/) is used to separate the results before and after cycle. For conciseness, only resistances are listed.

Resistance	LCP-pyrolysis	LCP-spray	LCP-deposition
R_s ($\Omega \text{ cm}^2$)	7.5/8.6	3.9/7.1	6.8/5.5
R_f ($\Omega \text{ cm}^2$)	285/302	136/143	99/118
R_{ct} ($\Omega \text{ cm}^2$)	103/97	81/90	61/52

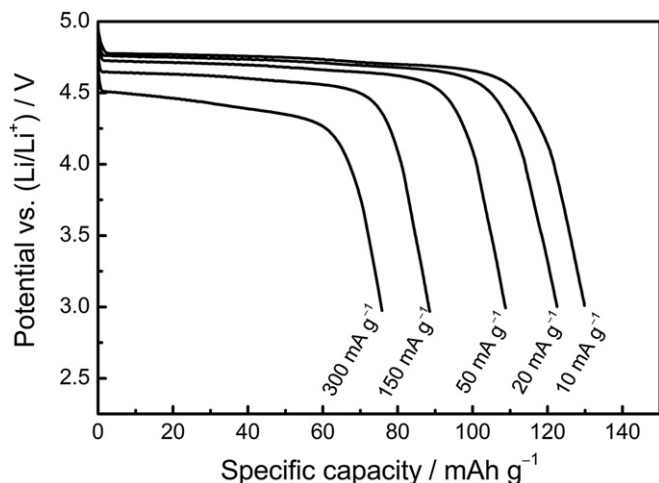


Fig. 11. The rate discharge capability of LCP-deposition.

performance cannot meet the requirement for high-power utilization, it is sufficient for stationary energy storage. Optimizations of particle size, morphology, and composition could further improve the power capability to meet versatile applications.

4. Conclusions

In summary, three techniques, i.e., pyrolysis, spray, and deposition were adopted for carbon coating on LiCoPO_4 particles, and their effects were compared. The results show that coating techniques determine the quality of carbon layer, and therefore affect the electrochemical performance of LiCoPO_4 . A uniform and compact carbon layer is critical to reducing the resistances and suppressing side reactions, therefore the modified electrode material has a larger capacity delivery and better cyclability. The vapor deposition process helps develop a homogeneous carbon coating layer on LiCoPO_4 , thus enables the active composite to deliver a high specific capacity of 130 mA h g^{-1} and maintain 80% of that after 30 cycles in the voltage range of 3.0–5.0 V.

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References

- [1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [2] S. Okada, S. Sawa, M. Egashira, J.-I. Yamaki, M. Tabuchi, H. Kageyama, T. Konishi, A. Yoshino, *J. Power Sources* 97–98 (2001) 430.
- [3] K. Amine, H. Yasuda, M. Yamachi, *Electrochem. Solid-State Lett.* 3 (2000) 178.
- [4] J.M. Lloris, V.C. Pe  rez, J.L. Tirado, *Electrochem. Solid-State Lett.* 5 (2002) A234.
- [5] W.C. West, J.F. Whitacre, B.V. Ratnakumar, *J. Electrochem. Soc.* 150 (2003) A1660.
- [6] N.N. Bramnik, K. Bramnik, T. Buhrmester, C. Baehtz, H. Ehrenberg, H. Fuess, *J. Solid State Electrochem.* 8 (2004) 558.
- [7] M. Nakayama, S. Goto, Y. Uchimoto, M. Wakihara, Y. Kitajima, *Chem. Mater.* 16 (2004) 3399.
- [8] M.E. Rabanal, M.C. Gutierrez, F. Garcia-Alvarado, E.C. Gonzalo, M.E.A. Dompablo, *J. Power Sources* 160 (2006) 523.
- [9] J. Wolfenstine, J. Read, J.L. Alen, *J. Power Sources* 163 (2007) 1070.
- [10] N.N. Bramnik, K. Nikolowski, C. Baehtz, K.G. Bramnik, H. Ehrenberg, *Chem. Mater.* 19 (2007) 908.
- [11] H.H. Li, J. Jin, J.P. Wei, Z. Zhou, J. Yan, *Electrochem. Commun.* 11 (2009) 95.
- [12] I. Taniguchi, T.N.L. Doan, B. Shao, *Electrochem. Acta* 56 (2011) 7680.
- [13] J.L. Shui, Y. Yu, X.F. Yang, C.H. Chen, *Electrochem. Commun.* 8 (2006) 1087.
- [14] I.C. Jang, C.G. Son, S.M.G. Yang, J.W. Lee, A.R. Cho, V. Aravindan, G.J. Park, K.S. Kang, W.S. Kim, W.I. Cho, Y.S. Lee, *J. Mater. Chem.* 21 (2011) 6510.
- [15] D.-W. Han, Y.-M. Kang, R.-Z. Yin, M.-S. Song, H.-S. Kwon, *Electrochem. Commun.* 11 (2009) 137.
- [16] F. Wang, J. Yang, Y. NuLi, J. Wang, *J. Power Sources* 195 (2010) 6884.
- [17] J.L. Allen, T.R. Jow, J. Wolfenstine, *J. Power Sources* 196 (2011) 8656.
- [18] C. Delacourt, C. Wurm, P. Reale, M. Morcrette, C. Masquelier, *Solid State Ionics* 173 (2004) 113.
- [19] M. Gaberscek, R. Dominko, M. Bele, M. Remskar, J. Jamnik, *Solid State Ionics* 177 (2006) 3015.
- [20] J. Ni, L. Gao, *J. Power Sources* 196 (2011) 6498.
- [21] F. Izumi, T. Ikeda, *Mater. Sci. Forum* 321–323 (2000) 198.
- [22] H. Ehrenberg, N.N. Bramnik, A. Senyshyn, H. Fuess, *Solid State Sci.* 11 (2009) 18.
- [23] R. Sharabi, E. Markevich, V. Borgel, G. Salitra, D. Aurbach, G. Semrau, M.A. Schmidt, N. Schall, C. Stinner, *Electrochem. Commun.* 13 (2011) 800.
- [24] H. Fujimoto, K. Tokumitsu, A. Mabuchi, N. Chinnasamy, T. Kasuh, *J. Power Sources* 195 (2010) 7452.
- [25] I.C. Jang, H.H. Lim, S.B. Lee, K. Karthikeyan, V. Aravindan, K.S. Kang, W.S. Yoon, W.I. Cho, Y.S. Lee, *J. Alloys Compd.* 497 (2010) 321.
- [26] J.-M. Atebamba, J. Moskon, S. Pejovnik, M. Gaberscek, *J. Electrochem. Soc.* 157 (2010) A1218.
- [27] J.Y. Song, H.H. Lee, Y.Y. Wang, C.C. Wan, *J. Power Sources* 111 (2002) 255–267.
- [28] H. Li, H. Zhou, *Chem. Commun.* 48 (2012) 1201.
- [29] F. Wang, J. Yang, P. Gao, Y. NuLi, J. Wang, *J. Power Sources* 196 (2011) 10258.